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From molecular aggregates to novel organosilicon and phosphorus/arsenic compounds*

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Abstract: Dimetalated primary silylphosphanes and related arsanes, respectively, can serve as versatile and symbiotic building blocks for the synthesis of unusual organosilicon- phosphorus/arsenic compounds. This has been shown through the metathesis reaction of dichlorodiorganosilanes with novel types of dilithium silylpnictide clusters to give silylidene-phosphanes and-arsanes ('phospha/arsa-silenes', Si=P and Si=As). Furthermore, other unusual types of novel dimetalated derivatives REM_2 (R = silyl; E = P, As; M = Li, Cu(I), Sn(II), Al(III)), including the valuable lithium tetraphosphinoalanate, are discussed which have been employed as remarkably soft reagents for transfer of R_2E^-, RE^{2-} and E^{3-} moieties and furthermore for the synthesis of metastable solids (Sn_2P).

INTRODUCTION

The nucleophilic transfer of phosphorus containing functional groups such as secondary alkali metal organophosphanides toward appropriate electrophiles (e.g. organoelement halides) is one of the most important methods to built-up defined tertiary organophosphorus ligands or to synthesize other main group element phosphanyl compounds. Usually, metalated secondary phosphanides are highly aggregated in solution as well as in solid state and their structures strongly influence reactivity and stereoselectivity in the desired nucleophilic substitution process. While the structure-reactivity relationships are best known for secondary phosphanide species [1], the knowledge about molecular dimetalated primary phosphanes, that is, dimetal phosphandiides and main group metal-rich phosphinidene clusters, respectively, is relatively scarce. However, there is a considerable demand for molecular dimetal pnictides for selective pnictogen transfer via metathesis reaction. Normally, alkyl- and arylphosphandiides and related arsandiides exist as polymeric insoluble solids which are less reactive and cannot be used for soft metathesis reactions [2]. We observed that the situation is drastically improved if primary triorganosilylphosphanes and -arsanes are employed and learned to utilize such starting materials for the synthesis of low-coordinated silicon-phosphorus and -arsenic compounds. The remarkably high solubility of dimetalated silylphosphanes and arsanes, respectively, is due to the lipophilic surface of the silyl substituent in the sphere of the globular clusters. Thus *molecular* dilithium silylphosphandiide aggregates are easily accessible through metalation of the respective primary silylphosphanes with lithium alkanides. Their different structures, depending on the nature of the metal and on the steric demand of the silyl group, imply different reactivity toward electrophiles as we have learned from the reaction toward dichlorodiorganosilanes.

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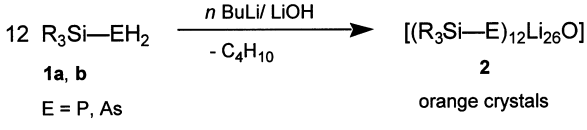
MOLECULAR DILITHIUM PHOSPHANDIIDE AND ARSANDIIDE AGGREGATES

Initial studies by Issleib & Tzschach in 1959 demonstrated that the metalation of primary organophosphanes with lithium alkanides and lithium phenylide affords dilithium phosphandiides, which were isolated as insoluble, amorphous solids [2]. The very high degree of aggregation is certainly responsible for the poor reactivity toward electrophiles. From the structural point they represent intermediates between the molecular compounds R_3P and the typical solid state compound Li_3P and it seems therefore interesting to determine the structural principles of this cluster type. Since lithium phosphanides form two-dimensional aggregates [3,4], one expects that dilithium phosphandiides will form three-dimensional clusters via Li-P linkages. As is known from many other types of ionogenic aggregates, the degree of aggregation is largely determined by steric demand, whereas the solubility is dependent on the lipophilicity provided by the organo groups. Triorganosilylphosphanes and -arsanes have been employed to enhance the solubility of the desired dilithium derivatives. Indeed, the double lithiation of the primary silylphosphanes **1a** and the analogous arsanes **1b** in the presence of LiOH (as a partial hydolysis product of *n* BuLi) results in the dodecameric clusters **2**, which can be easily recrystallized in aromatic solvents (Scheme 1) [5].



Scheme 1

The clusters have intriguing structures as shown for the dilithium arsandiide Li_2O adduct in Fig. 1. The compound consists of three shells of platonic units: The As centers form a As_{12} icosahedron, in which all of the 20 triangular faces are capped by a Li center. The Li_{20} centers thereby constitute a pentagondodecahedron as a dual polyhedral framework with approximately I_h point-symmetry. The remaining four Li centers are accommodated in the cavity of the approximately spherical $[As_{12}Li_{20}]^{4-}$ framework (diameter ≈ 8 Å) and bind to an encapsulated Li_2O molecule leading to the formation of a $[Li_6O]^{4+}$ octahedral core.

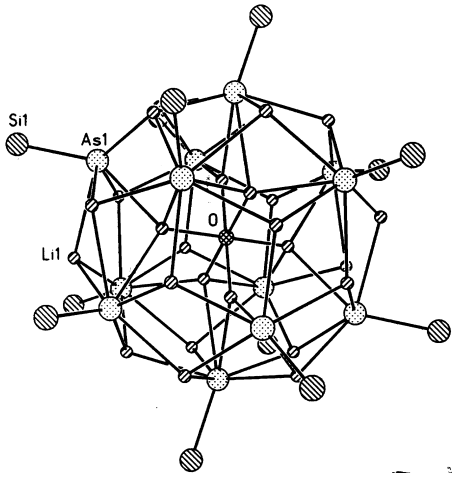


Fig. 1 Molecular structure of a dodecameric $Li_2As(SiR_3)$ cluster **2** with incorporated Li_2O [5]. The organo groups R have been omitted for clarity.

That the degree of association is dependent on the steric demand of the silyl groups has been demonstrated with the formation of an octameric species which bears very bulky Si*i*Pr_2(mesityl) groups [5]. Further increase of steric demand furnishes dimeric aggregates of which one example has been structurally characterized in the form of a fluorosilane complex [6]. One of the central questions concerning the structures of **2** seems the function of the incorporated lithium oxide molecule during the formation of the globular dodecamers. The first hint that Li_2O is probably not necessary for the

aggregation of 12 phosphanide/arsanide units stems from the formation of the Li_2O-free arsanide aggregate **3** which is formed during the partial metalation of a primary silylarsane. It consists of three equivalents of dilithium arsandiide and three equivalents of monolithium arsanide with an empty interior. The cluster can be transformed into the corresponding Li_2O-filled aggregate **2** (Fig. 2).

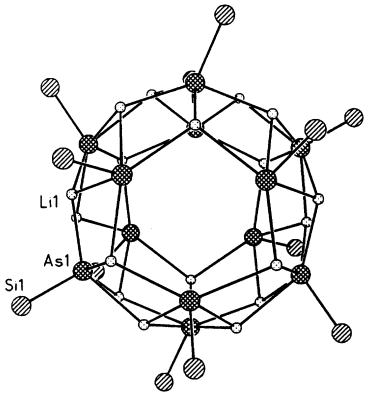


Fig. 2 Molecular structure of a partially metalated dodecameric silylarsane **3**: $[(R_3Si\text{-}AsLi_2)_6\ (R_3Si\text{-}AsHLi)_6]$. The organo groups R have been omitted for clarity.

The result of the metalation of silylphosphanes/arsanes in the absence of Li_2O is even more surprising; metalation with rigorously Li_2O-free tert-BuLi yields the first mixed-valent lithium-arsenic cluster **4** and molecular hydrogen is evolved. The elimination of H_2 clearly implies a redox process and therefore **4** is lithium-deficient and contains trivalent and monovalent arsenic centers. The cluster consists of 10 R_3Si-As units and 16 Li centers which form an ionogenic cluster-type like **2** and **3**. The structural principle resembles that of **2**, however, the As centers form a dicapped Archimedean antiprism in which all of the 16 triangular faces are capped with Li ions (Fig. 3).

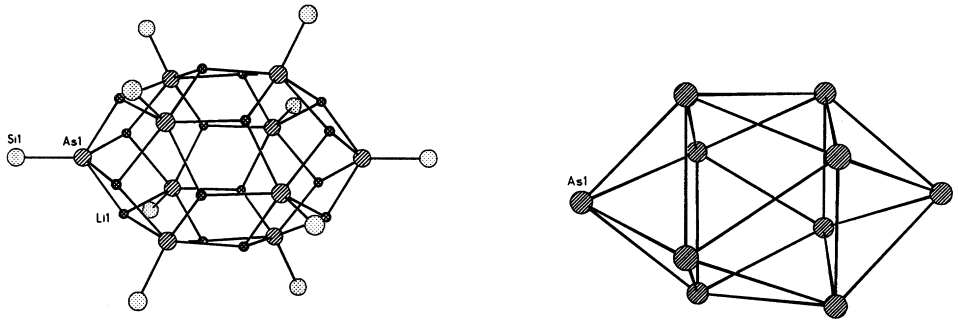


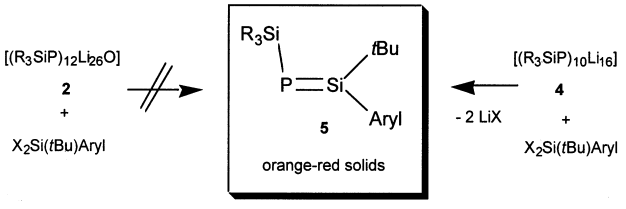
Fig. 3 Molecular structure of $[(R_3Si\text{-}As)_{10}Li_{16}]$ **4** (left) and As_{10} framework (right). The organo groups R are omitted for clarity.

The arrangement of the Li ions reveals two sets of chemically different silyl-arsenic units in the ratio of 4:1, whereas two sorts of lithium ions are observed in the ratio of 1:1. This has been unambiguously proven by CP-MAS solid-state NMR spectroscopy (^{7}Li, ^{29}Si) [7]. The structures of the novel electron deficient cluster **4** as well as the lithium oxide-containing clusters **3** show only a slight tendency to dissociate in solution as shown by cryoscopic measurements. One of the main differences between **2** and **4** is their distinctly different reactivity to serve as a RE^{2-} source (E = P, As).

METATHESIS REACTIONS TO PHOSPHASILENES

For the synthesis of fragile multiple bonds between phosphorus/arsenic and other heavy main group elements via metathesis routes, starting from dilithium pnictides and dihalogen-organoelement compounds, it is necessary to provide soluble dilithium pnictides which are reactive enough under

mild conditions so that the desired multiple bond (E = X) survives. It turned out that the reactivity of **2** toward dichlorodiorganosilanes in toluene is much lower than that of the unusual mixed-valent lithium-pnictogen aggregates **4**. In fact, whereas **2** reacts with the bulkily substituted dichloro(isityl)tert-butylsilane in toluene only above 110 °C with the formation of several products (no Si = P compound is formed), the same transformation with **4** as the RE^{2-} source instead of **2** gives the desired phosphasilene **5** at 80 °C in 55% yield. The lower reactivity of **2** compared with **4** is a result of the highly effective close packing of anionic and cationic centers. One can expect, that the synthetic capacity of **4** will be very useful for the synthesis of other low-coordinated element-phosphorus/arsenic compounds in near future (Scheme 2).



Scheme 2

STRUCTURAL CHEMISTRY OF COPPER (I)-AND TIN(II)-PHOSPHANDIIDES

Since dilithium pnictides of the type **2** prefer typical salt-like structures with close packing of the cationic (Li) and anionic centers (E = P, As, O) which makes the cluster frameworks quite stable, we investigated the influence of Cu^+ ions instead of Li^+ centers in the silylphosphandiide aggregate series. The first neutral copper phosphandiyl cluster **6** is formed through metalation of trialkylsilylphosphane with [(CuO *t*Bu)$_4$] [8]. The structure of the dark red compound **6** is very different from that of the corresponding dilithium salt **2** (Fig. 4).

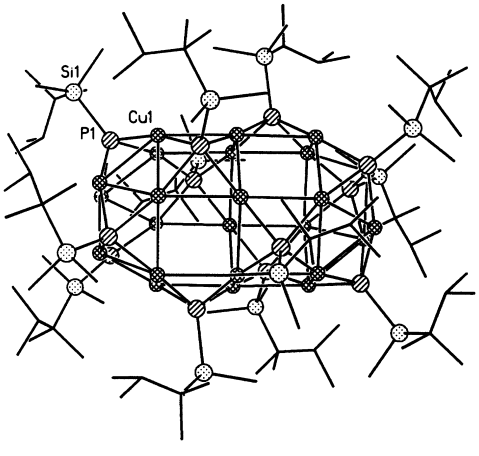


Fig. 4 Molecular structure of the dicopper phosphandiide dodecamer **6** (SiR_3 = $SiMe_2CMe_2iPr$). For details see [8].

The Cu_{24} cluster framework consists of five parallel Cu planes (Cu_3, Cu_6, Cu_6, Cu_6, Cu_3), while the 12 silylphosphanediyl fragments cap alternately the Cu_4 faces of the Cu_{24} polyhedron resulting in five-fold coordinated P centers. The different structures of **2** and **6** are due to the higher covalent character of the Cu-P bonds and dispersion-like interactions between the Cu centers. Apparently, the less polar character of **6** disfavors inclusion of Li_2O. The different bonding situation in **6** provides novel possibilities in selective nucleophilic transfer of phosphandiide groups. For example, two α-halogenated functionalized carbon hydrides can be linked via a phosphanediyl-bridge, whereby halogen centers are selectively replaced even if there are other reactive functional groups present (ester, nitro, etc.).

The relatively high acidity of the P-H bonds in primary silylphosphanes allows also stannylation reactions on phosphorus. In the case of tin(II) starting materials we used for such a metalation Lapperts

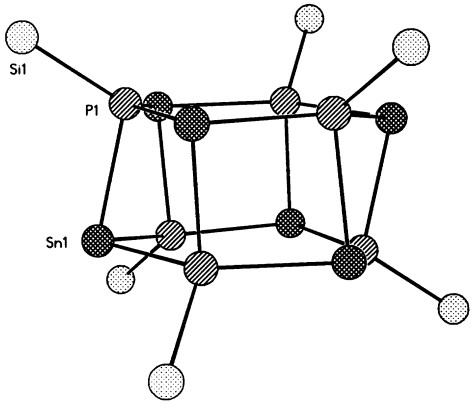


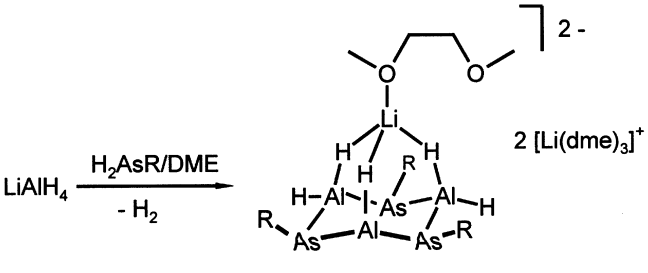
Fig. 5 Solid state structure of the tin(II) phosphandiyl cluster **7** [8]. The organo groups on silicon are omitted for clarity.

diaminostannanediyl derivative and prepared the first molecular tin(II) phosphandiyl cluster **7** having a Sn_6P_6 cluster skeleton [8] (Fig. 5).

The black crystals of **7** imply unusual electronic interactions between the tin(II) centers but the reason for its strong color is not well understood. The tin centers are suitable for a transmetalation reaction. For example, the stepwise transformation of **7** with barium metal in tetrahydrofuran furnishes mixed barium-tin phosphanediyl aggregates and the replacement of tin(II) by iron(II) through the reaction of **7** with $FeCl_2$ yields mixed ferromagnetic iron-tin phosphandiyl clusters. Compound **7** and related clusters are potential single source precursors for the synthesis of novel metastable solids. In fact, thermolysis of **7** at 330 K leads, under loss of the silyl groups, to a metastable tin-rich phosphide which has the approximate composition Sn_2P.

TETRAPHOSPHINO- AND TETRAARSINO-ALANATES: UNUSUAL PNICTOGEN TRANSFER REAGENTS

Lithium tetraphosphinoalanate is known to be a mild PH_2 transfer reagent with comparatively low basicity [9]. The latter property is important for the synthesis of multiple phosphinated/arsinated compounds. Since multiple phosphaneyl- and arsaneyl-substituted element hydrides of group 13 and 14 elements, $E_n(XH_2)_m$ (E = B, Al, Ga, In, Si, Ge, Sn; X = P, As), are important as starting materials for the preparation of optoelectronic materials, we have been very interested in the synthesis of multiple XH_2-substituted element hydrides, starting from the respective halide derivatives. Although the respective tetraphosphinoalanate and the tetraarsinoalanate are thermally fragile we carried out several PH_2- and AsH_2-transfer reactions [10,11]. Recently we achieved the synthesis of tetraphosphinosilane $Si(PH_2)_4$ and its germanium homologue, which are useful volatile precursors for the preparation of metastable Element 14-phosphides [11], from the reaction between $Si(Ge)Cl_4$ and $LiAl(PH_2)_4$. A single crystal of $Si(PH_2)_4$ suitable for X-ray structure analysis was obtained by *in situ* crystallization on a diffractometer at −30 °C. It is noteworthy that the compound forms inversion-symmetrical molecule pairs with two P-H-P interactions (Fig. 6).



Scheme 3

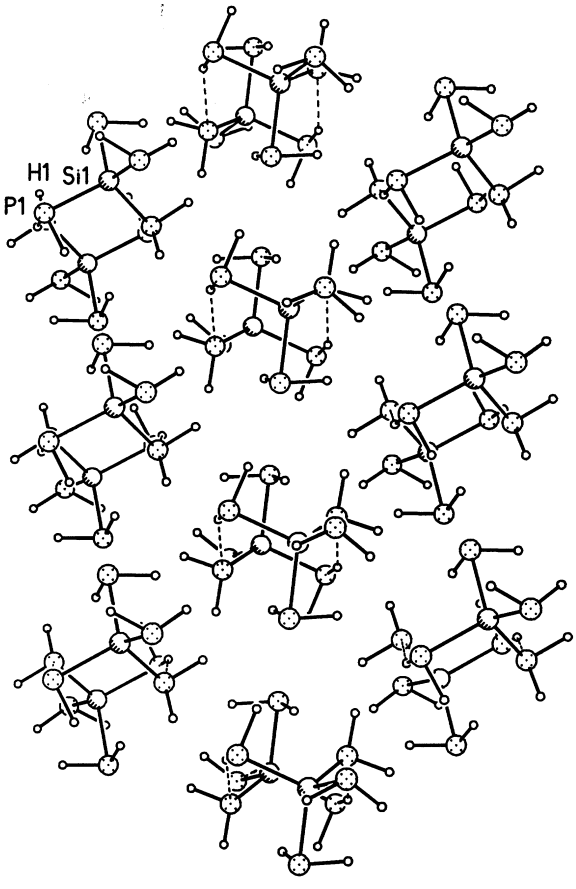
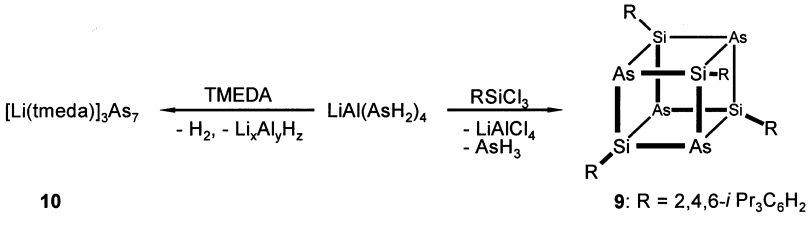


Fig. 6 Crystal packing diagram of $Si(PH_2)_4$. For details see [11].

Some hints about the fate of tetraphosphino- and tetraarsinoalanates and their decomposition products have been observed through the reaction of primary silylphosphanes and -arsanes, respectively, with $LiAlH_4$ in 1,2-dimethoxyethane. In the case of primary silylarsanes, the latter process leads to the expected tetraarsinoalanate (molar ratio arsane:alanate = 4:1), whereas its reaction with lithium alanate in the molar ratio of 1:1 furnishes the unusual triple ion pair **8** (Scheme 3) [10].

The synthetic potential of the lithium tetraarsinoalanates is further impressively demonstrated by the reaction with trichloroarylsilanes which leads to the first tetrasilatetraarsacubane derivatives **9**, and the tetramethylethylenediamine (tmeda)-induced decomposition of $LiAl(AsH_2)_4$ which furnishes, with the loss of H_2 and the formation of unknown lithium aluminium hydride complexes, the molecular Zintl compound **10** (Scheme 4) [10].



Scheme 4

These results clearly underline the synthetic potential of tetraarsinoalanates as a starting material for the synthesis of metastable solids and as a transfer reagent for the As^{3-} moiety.

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